

# Photosynthetic Accessory Pigments: Evidence for the Influence of Phycoerythrin on the Submarine Light Field

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Oceanic phytoplankton chlorophyll is known to produce a very significant influence on the optical properties of the ocean. The chlorophyll-driven optical properties are in fact so strong as to allow global satellite mapping of the pigment concentration in the upper ocean using upwelled water-leaving radiances. In this paper, extensive experimental evidence is presented to strongly suggest that upwelled water-leaving spectral radiances (and therefore the submarine light field source) also include physical scattering and absorption effects of photosynthetic accessory pigments such as phycoerythrin. In the water column, the presence of phycoerythrin was measured over wide regions of the ocean using well-established airborne laser-induced spectral fluorescence techniques. Active-passive correlation spectroscopy methods revealed that concurrently measured water-leaving spectral radiances in the  $\sim 600$  nm spectral region were highly correlated with the laser-induced phycoerythrin pigment fluorescence. The analysis was performed on data sets in which the phycoerythrin

and chlorophyll fluorescence were not coherent in order to permit the unambiguous evaluation of results.

## INTRODUCTION

The chlorophyll pigment found in marine phytoplankton dominate the optical properties of the world's oceans. This is amply demonstrated by the fact that a) the in-water diffuse attenuation coefficient for downwelling spectral irradiance and the chlorophyll-like pigment concentration can be directly related to each other through optical models (Smith and Baker, 1978) and b) the in-water radiant energy scattered toward the zenith (water leaving radiance) can be detected by satellite multispectral sensors and used for global mapping of chlorophyll pigment concentration (Gordon and Morel, 1983). To date, chlorophyll (and chlorophyll-like material) is the only phytoplankton component specifically linked to ocean color spectral variability (Smith and Baker, 1978; Morel and Prieur, 1977). There are a number of other constituents in the water column (Gordon and Morel, 1983) and within marine phytoplankton (Bidigare et al., 1985; Gieskes and Kraay, 1983) that can

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Received 15 March 1990; revised 6 September 1990.

contribute to the spatial (Esaias et al., 1986) and spectral (Hoge and Swift, 1986a) variability of the color of the ocean. However, the specific influence of each of these other constituents, such as phycoerythrin, on the marine light field may be masked by the dominating effect of the chlorophyll pigment and/or spectral overlap with each other. Phycoerythrin is an important accessory pigment to chlorophyll in marine phytoplankton and is one of the major light-harvesting elements for photosynthesis in the cyanobacteria, rhodophytes, and cryptophytes (Glover, 1985; hEocha, 1962; Cohen-Bizire and Bryant, 1982; Yentsch and Phinney, 1985; Exton et al., 1983).

The photosynthetic accessory pigments do not influence the in-water spectral radiances and irradiances quite so profoundly as does chlorophyll *a*. This situation is indicated by the fact that, despite thousands of measurements of the spectral characteristics of the submarine light field, there have been no reports of the presence of the phycobilin pigments within the spectra (Lewis et al., 1986). Problems in determining the spectral manifestation of phycobilin pigments arise in part due to the difficulty of extracting and quantitatively measuring pigments such as phycoerythrin at the same time that the spectral properties are being measured. A technique for extraction of the phycoerythrin pigment has only recently been published in the scientific journals (Stewart and Farmer, 1984) and methods for using standard flow-through fluorometers to measure phycoerythrin pigment fluorescence aboard research vessels have not been satisfactorily developed (R. C. Smith, Univ. of California, Santa Barbara, private communication).

The lack of definition of the effects of phycoerythrin on the marine light field is not surprising since the discovery, widespread existence (Waterbury et al., 1979; 1986), and physiological competence of some phycoerythrin-bearing organisms have only recently been reported (Li et al., 1983; Platt et al., 1983). However, interest in phycoerythrin and the role of this pigment in total ocean productivity and in the fundamentally important carbon and nitrogen biogeochemical cycles has been increasing. The measurement of phycoerythrin fluorescence is quite feasible since the fluorescence cross section has been roughly estimated to be an order of magnitude higher than that of chlorophyll (Houghton et al., 1983). The recent reports of HPLC measurements of other phytoplankton constituents also provides optimism

for the increased availability of phytoplankton pigment data to accompany shipboard measured spectral data (Bidigare et al., 1985; Gieskes and Kraay 1983). The development of fluorometers which use a laser excitation source for stimulating phycoerythrin fluorescence could provide underway measurements of the distribution of this photopigment.

Knowledge of the influence of accessory pigments on the submarine light field is important for several reasons. First, primary production is driven by the submarine light field. If phycobilipigments are influencing the submarine light field, then they must be absorbing significant amounts of radiation useful to the photosynthetic process and to primary production in general. [The degree to which the absorbed radiation is efficiently converted to useful fixation of carbon is, of course, arguable since phycoerythrin expels considerable fluorescent energy in the 560–578 nm bands (Alberte et al., 1984; Houghton et al., 1983).] However, laboratory cultures have shown that intracellular phycobiliproteins in cyanobacteria increase as a response to low light levels (Kana and Glibert, 1987; Wyman et al., 1985; Barlow and Alberte, 1985), thus increasing the absorption cross section of the cell. Second, the primary production capacity of the phytoplankton ensemble is altered by the extent to which the underwater light field is absorbed or scattered (for example, by a phycobilin chromophore). These photons are a) removed from further direct use or b) wavelength-shifted via fluorescence and Raman emission to wavelengths more (or less) useful to other pigments such as chlorophyll, carotenoids, or other accessory pigments. Third, phycobilin-modified upwelled spectral radiances can cause errors in the measurement of chlorophyll since, for example, the usual 550 nm chlorophyll remote sensing band on the Coastal Zone Color Scanner (CZCS) could contain signal from an interfering accessory pigment (phycoerythrin). Fourth, if the phycobiliproteins influence the submarine light field, then resulting upwelled radiances (that ultimately leave the water and enter the atmosphere and space) can then be detected and used for spaceborne satellite measurement of the pigment. Fifth, the optical variability can affect oceanic heat budgets (Marra and Hartwig, 1984).

It is the purpose of this paper to present experimental field evidence that strongly suggests that phycoerythrin influences the underwater light field and the resulting upwelling, water-leaving

radiance. For Case 1 (Gordon and Morel, 1983) waters, some limited evidence for the influence of phycoerythrin on the submarine light field has already been given (Hoge and Swift, 1986a) together with the initial technical details of the active-passive correlation spectroscopy (APCS) methodology used to study ocean color variability (Hoge and Swift, 1987). The results presented in this paper provide some additional Case 1 field observations but principally address Case 2 (Gordon and Morel, 1983) waters and the diverse and highly variable biooptical properties that exist there. These additional findings serve to complement and expand the previous Case 1 findings (Hoge and Swift, 1986a) and, as more applicable field data is obtained in the ensuing field missions, it too will be presented to further the understanding of the influence of the accessory pigments upon the underwater light field.

The spectral composition of the underwater light field is determined by the penetrating solar irradiance as well as absorption and scatter by phytoplankton, water molecules, and dissolved and entrained particulate matter. The submarine spectral radiant energy scattered in such a way that it

escapes the surface on an upward path (and is thus "backscattered" or "upwelled") maintains the spectral signature of the suspended and dissolved material in the ocean volume. Thus a study of the water-leaving radiances allow one to gain information about the materials in the water volume (Smith and Baker, 1978). These latter up-welled spectral radiances will be used to infer the influence of phycoerythrin on the submarine light field when the pigment is being concurrently measured within the water column by established airborne laser-induced fluorescence methods.

The mathematical nomenclature and physical measurement units to be used in this paper are defined and described within Table 1.

## INSTRUMENTATION AND AIRBORNE FIELD EXPERIMENTS

The Airborne Oceanographic Lidar (AOL) and its integral passive ocean color subsystem (POCS) (Hoge et al., 1986a,b) were used to obtain the water-leaving radiances and the in-water phycoerythrin and chlorophyll fluorescence data pre-

Table 1. The Mathematical Symbols, Their Descriptions, and Physical Measurement Units Used within This Paper

Symbol	Description	Units
$\lambda_j$	wavelength of $j$ th spectral channel	nm
$\rho_p(\lambda_j)$	correlation value of passively derived phycoerythrin with center band of curvature algorithm at $\lambda_j$ ; similar definition for chlorophyll, $\rho_c(\lambda_j)$	unitless; values between -1 and +1
$L(\lambda_i)$	water-leaving radiances obtained from airborne sensor radiances by the subtraction of reflected sky radiances; at 150 m flight altitude, the atmospheric path radiance is ignored	$\mu\text{W}/\text{cm}^2 /$ $\text{sr}/\text{nm}$
$\Delta_\omega(\ )$	difference operator defined by $\Delta_\omega f(\lambda) = f(\lambda + \omega/2) - f(\lambda - \omega/2)$	unitless
$G_\omega(\lambda_i)$	defined by Eq. (3) in text	unitless
$F'(\lambda_i)$	pigment fluorescence $F(\lambda_i)$ divided or normalized by the water Raman signal $F(\lambda_R)$ , i.e., $F'(\lambda_i) \equiv F(\lambda_i)/F(\lambda_R)$	dimension ratio
$a, b$	linear regression constants in a chlorophyll algorithm such as $c = aG^{-b}$ ; similar but not identical definitions for $A, B$ and $\alpha, \beta$	vary according to algorithm
$P$	phycoerythrin pigment concentration	$\mu\text{g}/\text{L}$
$c$	chlorophyll pigment concentration	$\mu\text{g}/\text{L}$

Table 2. Identification of the Field Experiment Location and Date, Water Type, and Mission Configuration and Associated Information

Flight line	Water Class	Flight Type	Flight Date	Associated Oceanographic Experiment	Viewing Angle	References
A	Case II	transit	8/18/84	CZCS-3 Calib.	15° off nadir	Hoge et al., 1987
B	Case II	transit	8/17/84	CZCS-2 Calib.	15° off nadir	Hoge et al., 1987
C	Case I	mapping	8/12/84	SEEP <sup>a</sup>	15° off nadir	Hoge and Swift, 1986a, b; Hoge and Swift, 1987
D	Case II	system test and evaluation	8/21/87	BIOWATT	nadir	Marra and Hartwig, 1984

<sup>a</sup>SEEP = Shelf Edge Exchange Processes.

sented here. The AOL instrumentation has been discussed in detail in papers dealing with various marine applications including other chlorophyll mapping field experiments (Hoge and Swift, 1981a, b; 1983; 1985; Smith et al., 1987). The wide range of other possible oceanic and terrestrial applications of an airborne lidar have already been given (Hoge, 1988) and will not be listed here. The POCS instrumentation subsystem has been recently described in detail (Hoge et al., 1986a). Its application to the airborne measurement of

oceanic pigments has also been given (Hoge et al., 1986b). The principal hardware features of the AOL-POCS and their combined operation in an active-passive mode have been presented (Hoge et al., 1986a, b) together with applications to ocean color spectral variability (Hoge and Swift, 1987), satellite color sensor band evaluation (Hoge and Swift, 1986b), and radiance ratio algorithms for Case II waters (Hoge et al., 1987). The system acquires active-passive ocean color data which was utilized to investigate the phycoerythrin in-

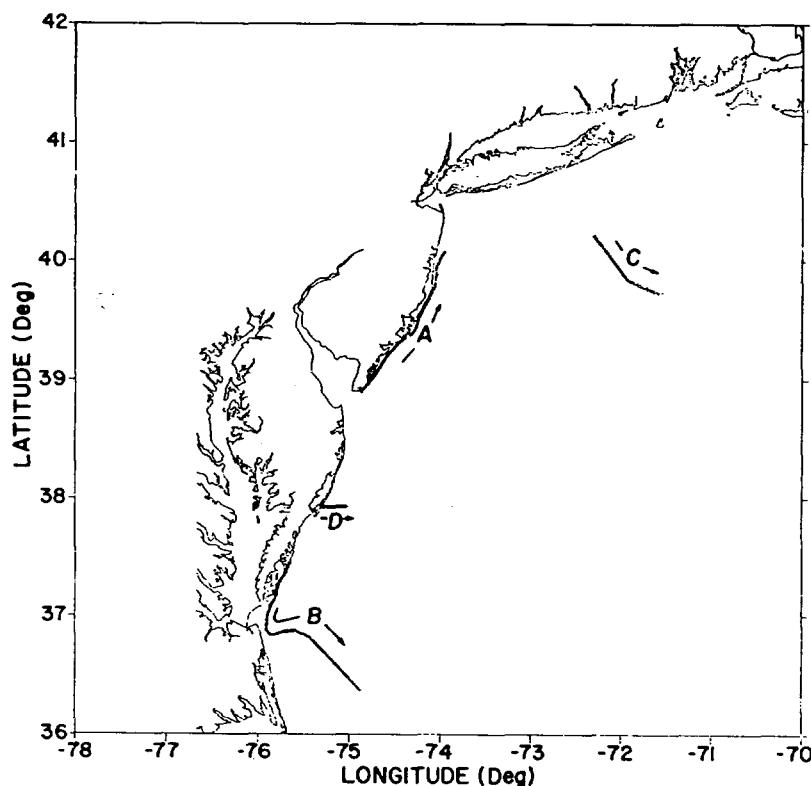


Figure 1. Map showing the geographical locations of flight lines selected for analysis in this phycoerythrin study. The aircraft flight direction is indicated by arrows.

fluence by using a highly effective technique known as active-passive correlation spectroscopy (Hoge and Swift, 1986a).

The data used for the phycoerythrin analyses were obtained during four separate airborne field missions conducted over the Atlantic Ocean east of the United States in 1984 and 1987. All but one of these data sets were obtained either on test and evaluation flights or on transit legs to the actual field experiment sites. We will simply designate the separate airborne mission flight lines as Flight Lines A, B, C, and D. Table 2 provides the major field experiment associated with each of these flight lines, the type of flight, the water type, and references that the reader may wish to consult for additional information about the overall scientific objectives of the oceanographic experiment. None of the field experiments had as their objective the determination of the influence of phycoerythrin on the submarine light field. Thus, more optimum data can probably be obtained on missions dedicated to passive pigment detection. As will be discussed in the next section, many flight lines had to be evaluated in order to select those suitable for analysis. The locations of Flight Lines A, B, C, and D are shown in Figure 1. All flight lines are located in Case II waters except for Flight Line C (Hoge and Swift, 1987).

#### AIRBORNE DATA ACQUISITION, EVALUATION, AND PREPROCESSING

Recently, airborne laser systems have demonstrated that chlorophyll *a* and phycoerythrin fluorescence along with laser-induced water Raman backscatter can be reliably measured over wide areas of the ocean, both rapidly and at a high sample density (Hoge and Swift, 1981a; 1985; Hoge et al., 1986a,b). Hardware improvements to the AOL have enabled the instrument to acquire simultaneous active and passive ocean color measurements (Hoge et al., 1986a,b). During the past several years a large volume of data containing laser-induced and solar-induced spectra have been acquired while participating in major oceanographic field experiments. These paired active and passive spectral observations, obtained from the same footprints, permit advanced studies of the variability in ocean color spectral radiances (Hoge and Swift, 1987) and the development of algo-

rithms for the detection and measurement of fluorescing constituents in the upper layer of the ocean. A typical airborne flight mission produces ~ 50,000 pairs of active-passive observations.

Prior to selection for analysis with the active-passive correlation spectroscopy technique, the data from many flight lines were first evaluated for several important criteria. Specifically, these criteria were:

1. The active-passive correlation spectroscopy (APCS) technique uses a linear regression process to evaluate the results. Linear regression requires a reasonable range in the laser-induced pigment fluorescence to yield an accurate solution. Only those flight lines that provide a relatively wide range of phycoerythrin fluorescence were utilized in the analysis.
2. Very often the phycoerythrin fluorescence covaries with the chlorophyll fluorescence. In order to assure that the passive phycoerythrin algorithms are not responding to chlorophyll, only flight lines having segments of noncoherent chlorophyll and phycoerythrin fluorescence were considered for analysis.
3. Flight lines having some small scale phycoerythrin fluorescence variability or "patchiness" were selected. The relatively small, 1–10 km patches of elevated phycoerythrin concentration provide excellent visual contrast between profiles of laser-induced phycoerythrin fluorescence and estimates of phycoerythrin concentration developed following the application of the active-passive correlation spectroscopy technique.
4. Only glint-free data can be used for analysis. Data found to meet the first three criteria above were then edited to remove spectra contaminated with sun glint. Then, only passes requiring the removal of 10% or fewer observations were ultimately used for analysis.
5. The passive water-leaving spectral radiances must be tested to insure that no residual reflected sky radiance and path radiance remain in the data. This is done by testing the passive spectra for the recovery of chlorophyll using the spectral curvature algorithm (Campbell and Esaias, 1983). If application of the APCS method reveals that reasonably high correlation exists between the laser-induced chloro-

phyll fluorescence and curvature algorithms applied to blue and/or red radiances, then the passive spectra are assumed to be essentially free of unwanted radiation and ready for phycoerythrin analysis.

During the various flight missions a considerable amount of active and passive data was acquired. However, only a relatively small subset was found to meet all the above criteria for use in the analyses.

The data used for analysis were subjected to a simple average over each 1.5-s interval prior to processing. This averaging was done to reduce the volume of samples and to smooth high frequency variability. The active and passive ocean color observations were each acquired at 6.25 samples/s on Flight Lines A, B, and C and at 10 samples/s on Flight Line D. Passive ocean color spectra containing sun glint were removed prior to the averaging. At the nominal 100 m/s velocity of the aircraft, this process effectively averages the samples obtained over a space of  $\sim 150$  m. A more comprehensive treatment of the data handling can be found in a recent paper (Hoge and Swift, 1983).

## ACTIVE-PASSIVE CORRELATION SPECTROSCOPY METHODS

### The Passive Ocean Color Spectrum

The solar-stimulated ocean color reflectance spectrum is not distinguished by numerous or prominent spectral features due to the phycoerythrin pigment. Rather, the most obvious characteristics of ocean color spectra are those induced by chlorophyll: a) the slope change in the nominal 450–570 nm region (Smith and Baker, 1978), b) the spectral flattening in the 450–510 nm section (Campbell and Esaias, 1983), and c) the fluorescence emission in the 675–695 nm segment (Neville and Gower, 1977). These attributes of the ocean color spectrum are so assertive that chlorophyll (and phaeopigments) can be remotely sensed using band ratios (Hoge et al., 1987), spectral curvature (Campbell and Esaias, 1983; Hoge and Swift, 1986b; 1987), and the amplitude of solar-induced spectral fluorescence emission (Neville and Gower, 1977). Since no obvious spectral characteristics have been reported for phycoerythrin, then very sensitive detection methods must be used.

We have found spectral curvature (Grew, 1981; Campbell and Esaias, 1983; Hoge and Swift, 1986a) techniques to be among the most responsive procedures available. Accordingly, it will be the principal analytical tool used herein. Radiance ratio algorithms have not exhibited as much detection sensitivity as curvature methods for the detection of the effects of phycoerythrin in the upwelled radiances.

### The Active or Laser-Induced Ocean Color Fluorescence Spectrum

Previous papers have presented typical airborne fluorescence spectra (Hoge and Swift, 1981a,b; 1985) resulting from pulsed laser stimulation at 532 nm. By contrast to passive ocean color spectra, the laser-induced fluorescence spectra are distinguished by rather narrow, identifiable spectral lines due to phycoerythrin and chlorophyll fluorescence, water Raman scatter, as well as the 532 nm laser backscatter from the water column. The water-Raman line is used to normalize the phycoerythrin band (and the chlorophyll band) to reduce effects on the levels of phycoerythrin and chlorophyll fluorescence due to spatial variability in the attenuation properties of the upper water column (Bristow et al., 1981; Hoge and Swift, 1981b). All correlation analyses were performed with the normalized phycoerythrin spectral line.

## ACTIVE-PASSIVE CORRELATION SPECTROSCOPY

Active-passive correlation spectroscopy (APCS) is a highly sensitive technique which allows subtle constituent-driven variations in the airborne ocean color spectrum to be easily detected (Hoge and Swift, 1986a). The details of active-passive correlation spectroscopy (APCS) have been given in previous papers dealing with its application to ocean color algorithm wavelength selection (Hoge and Swift, 1986a; Hoge et al., 1987). The reader should consult those papers for other a) instrumentation details, b) active-passive correlation spectroscopy methodology used with the ocean color spectral curvature algorithm, and c) the initial limited examples of phycoerythrin manifestations within ocean color radiances acquired in Case I waters (Hoge and Swift, 1986a). A brief

description of the APCS technique used in the analysis presented in this paper is given below.

During post-flight analysis, all possible sequential curvature ratios from the 32 available passive color bands of the AOL/POCS instrument are used to compute independent phycoerythrin concentration estimates. (The actual methodology is presented in more detail in the following section.) Each of the resulting curvature ratios are then linearly regressed against the corresponding laser-induced and water-Raman-normalized phycoerythrin fluorescence value along the entire flight line. High correlation coefficients ( $\rho > 0.80$ ) reveal those regions of the spectrum, where the ocean color spectral variability is strongly correlated with phycoerythrin fluorescence.

#### Validity of Airborne Active-Passive Methods

The airborne laser-induced chlorophyll fluorescence from the water column has been shown to yield high correlation with the chlorophyll pigment concentration derived by shipboard extractions and underway fluorescence measurements (Bristow et al., 1981; Hoge and Swift, 1981a; Walsh et al., 1986; Smith et al., 1987). The high correlations of laser-induced chlorophyll fluorescence with pigment extractions are found in spite of known photoplankton chlorophyll fluorescence variability caused by ambient light and nutrient changes. Regrettably, no phycoerythrin pigment extractions are available with which to compare our airborne phycoerythrin fluorescence findings. There is little doubt that phycoerythrin pigment is being detected since its spectral peak in the  $\sim 580$  nm region is routinely observed especially in the Middle Atlantic Bight (Hoge and Swift, 1983; 1986). Thus, under the assumption that the airborne laser-induced phycoerythrin fluorescence is a reliable indicator of the phycoerythrin pigment concentration, it will be used as the sole source for identification and evaluation of in-water and upwelled spectral variability attributable to phycoerythrin.

During the APCS processing each three-band curvature combination is linearly regressed with the water Raman normalized phycoerythrin and chlorophyll fluorescence measurements resulting in spectral correlation functions denoted as  $\rho_p(\lambda_j)$  or  $\rho_c(\lambda_j)$ , where  $\lambda_j$  is the wavelength of the  $j$ th band of the passive spectrometer. Typically from

5000 to 10,000 pairs of active and passive waveforms are obtained during the traversal of a single flight line of approximately 100 km in length. The spectral correlation  $\rho_p(\lambda_j)$  or  $\rho_c(\lambda_j)$  are usually produced from data acquired along a single flight line. The influence of phycoerythrin (or of chlorophyll) on the upwelled spectral radiances is readily identified in the correlation spectrum. Flight lines yielding absolute correlation values above  $\rho = 0.8$  are selected for further study. The effectiveness of algorithm bands is then qualitatively judged by visually comparing along-track profiles of the active pigment concentration with the passively derived estimates. The details of this procedure together with examples of the results are provided in the remaining sections.

#### APPLICATION OF ACTIVE-PASSIVE CORRELATION SPECTROSCOPY TO PHYCOERYTHRIN-INDUCED OCEAN COLOR SPECTRAL VARIABILITY

It would be desirable to use the unprocessed passive ocean color spectra  $L(\lambda_i)$  to derive pigment concentration values. Unfortunately, the high variability of the entire spectral waveform completely masks the desired, subtle color variations impressed upon the clear ocean water spectrum by the phycoerythrin pigment. To obtain useful information on the effects of phycoerythrin on the acquired radiances, the spectra must be processed using more sensitive techniques such as radiance ratios (Gordon and Morel, 1983; Hoge et al., 1987) or by spectral curvature (Grew, 1981; Campbell and Esaias, 1983; Hoge and Swift, 1986a). The curvature spectrum (which is related to the second derivative  $d^2S(\lambda_i)/d\lambda^2$ ) methods are quite sensitive and yield results which are reasonably free of unwanted environmental factors (Campbell and Esaias, 1983). The curvature algorithm is essentially a difference operator applied twice to the logarithm of the radiance in the middle spectral band. There are several important consequences of using this algorithm: 1) Since the spectral differences are usually small relative to the large radiance values involved, the leveraging imposed by the form of the algorithm necessitates high sensor precision and stability; 2) the calibration of the spectral radiance of the sensor is not a requirement, although mission to mission stability is es-

sential if the constants in Eq. (4) are to become anchored for real-time use; and 3) the algorithm may be applied in real time to ocean color spectra obtained at relatively low altitudes without serious consequences from atmospherically related effects (Campbell and Esaias, 1983). (Of course, at high altitudes, additive, independently varying, atmospheric path radiance must be removed before further processing with the three-band algorithm.) With these considerations in mind, we chose to process the passive color data with a curvature algorithm. The algorithm chosen is essentially that of Campbell and Esaias (1983)  $\Delta_\omega^2 \log S(\lambda_i)$ , where  $\Delta_\omega(\ )$  is a difference operator defined by

$$\Delta_\omega f(\lambda) = f(\lambda + \omega/2) - f(\lambda - \omega/2). \quad (1)$$

If  $\omega = 30$  nm and the operator is applied twice as required, Campbell and Esaias (1983) showed that

$$\Delta_\omega^2 \log L(\lambda_i) = -\log G_\omega(\lambda_i), \quad (2)$$

where

$$G_\omega(\lambda_i) = \frac{L^2(\lambda_i)}{L(\lambda_i + 30) \cdot L(\lambda_i - 30)}. \quad (3)$$

Thus, the processing of the  $L(\lambda_i)$  spectra is performed by starting with data from the bluest spectral band of the instrument,  $L(\lambda_i - 30)$ , then selecting data from the spectral position 30 nm redder,  $L(\lambda_i)$ , and another 30 nm to the red,  $L(\lambda_i + 30)$ . These three spectral radiances are used to compute  $G_\omega(\lambda_i)$  via Eq. (3).

The index label is changed to  $j$  in order to identify the fact that the original 32 spectral bands were first linearly interpolated to "create" additional bands separated by one nanometer instead of 11.25 nm as actually provided in the passive ocean color subsystem (POCS) of the AOL. The resultant interpolated bands are, in fact, composed of varied ratios between adjacent 11.25 nm wide spectral bands of the POCS and the resulting bands used in our calculations are thus effectively 22.5 nm in width. Although this method of data handling may be less than desirable for some analytical applications, our intent here is only to demonstrate that phycoerythrin has a measurable effect on the ocean color spectrum. It is not the purpose of this paper to derive specific algorithms for the actual measurement of phycoerythrin.

During this analytical procedure, the  $\lambda_j$  are successively incremented by 1 nm and the calculation is repeated until a complete curvature spec-

trum is obtained. For the actual data set to be discussed herein, the typical procedure is started at 443 nm and executed 288 times until the final curvature value is obtained from the raw radiances at 701 nm, 731 nm, and 761 nm. The "curvature spectrum,"  $G_\omega(\lambda_j)$ , is thus shorter than the spectral radiance  $L(\lambda_i)$  by 60 nm (30 nm each on the blue and red ends). A curvature spectrum is produced from each raw spectrum  $L(\lambda_i)$ . Linear correlation coefficients are then developed using  $-\log G_\omega(\lambda_j)$  versus  $F'(\lambda_i)$ , where  $F'(\lambda_i)$  is the laser-induced fluorescence at wavelength  $\lambda_i$  and where  $i$  corresponds to phycoerythrin wavelength  $\lambda_p$  (or chlorophyll wavelength  $\lambda_c$  if desired). The laser-induced phycoerythrin fluorescence is assumed to be linearly related to the phycoerythrin pigment concentration. We chose an algorithm of the form

$$P = A - B \log G_\omega(\lambda_j), \quad (4)$$

where  $P$  is the relative concentration of phycoerythrin (or chlorophyll). This form has been found to produce more consistent results in our work than the formulation used by Campbell and Esaias (1983),

$$\log P = a - b \log G_\omega(\lambda_m) \quad (5)$$

or the form by Grew and Mayo (1983) and Grew (1981),

$$\log P = \alpha - \beta G_\omega(\lambda_m), \quad (6)$$

where  $\lambda_m$  is 490 nm and  $A$ ,  $B$ ,  $a$ ,  $b$ , and  $\alpha$ ,  $\beta$  are the linear regression coefficients of all the respective forms.

Our choice of algorithm in (4) would not be expected to significantly alter our phycoerythrin findings since all three forms of the algorithms have in the past produced quite good correlation with chlorophyll measurements (Hoge et al., 1986b; Grew, 1981; Campbell and Esaias, 1983). Of course,  $G_\omega(\lambda)$  is common to all the algorithms in (4), (5), and (6).

Campbell and Esaias (1983) found that the curvature algorithm effectively eliminates variations due to changes in incident irradiance while at the same time enhancing spectral features of the water medium. Utilizing a model based on earlier work by Smith and Baker (1978), Campbell and Esaias (1983) were able to show that the irradiance reflectance of ocean water exhibits a distinctive curvature spectrum with a large nega-

tive curvature centered at 490 nm. As chlorophyll-like pigments are added to the water, this negative curvature monotonically approaches zero. This latter feature is the fundamental physical basis for the high sensitivity of the algorithm to chlorophyll in water. Analogously, we will use the algorithm for phycoerythrin and further demonstrate that the occurrence of increasing amounts of phycoerythrin pigment yield strong spectral curvature responses centered at  $\sim 600$  nm.

An example of a phycoerythrin spectral correlation function  $\rho_p(\lambda_i)$  generated by these APCS methods is shown in Figure 2a and a corresponding chlorophyll spectral correlation function in Figure 2b. These correlation functions were obtained from data acquired along Flight Line C as

more fully discussed in the following section. The phycoerythrin correlation peak in the  $\sim 600$  nm spectral region is of specific interest in this paper. This phycoerythrin correlation peak, when found in specific data sets, most often occurs when the chlorophyll influence at  $\sim 600$  nm is diminished as indicated by a low chlorophyll correlation value at this wavelength in Figure 2b. Frequently, but not always, when the chlorophyll dominance is found to be diminished at  $\sim 600$  nm, the phycoerythrin influence is allowed to emerge.

At this time a physical basis for the  $\sim 600$  nm peak in the phycoerythrin correlation spectrum is difficult to identify since the *in vivo* phycoerythrin fluorescence occurs at 570–580 nm (Exton et al., 1983) and its absorption (excitation) maximum is

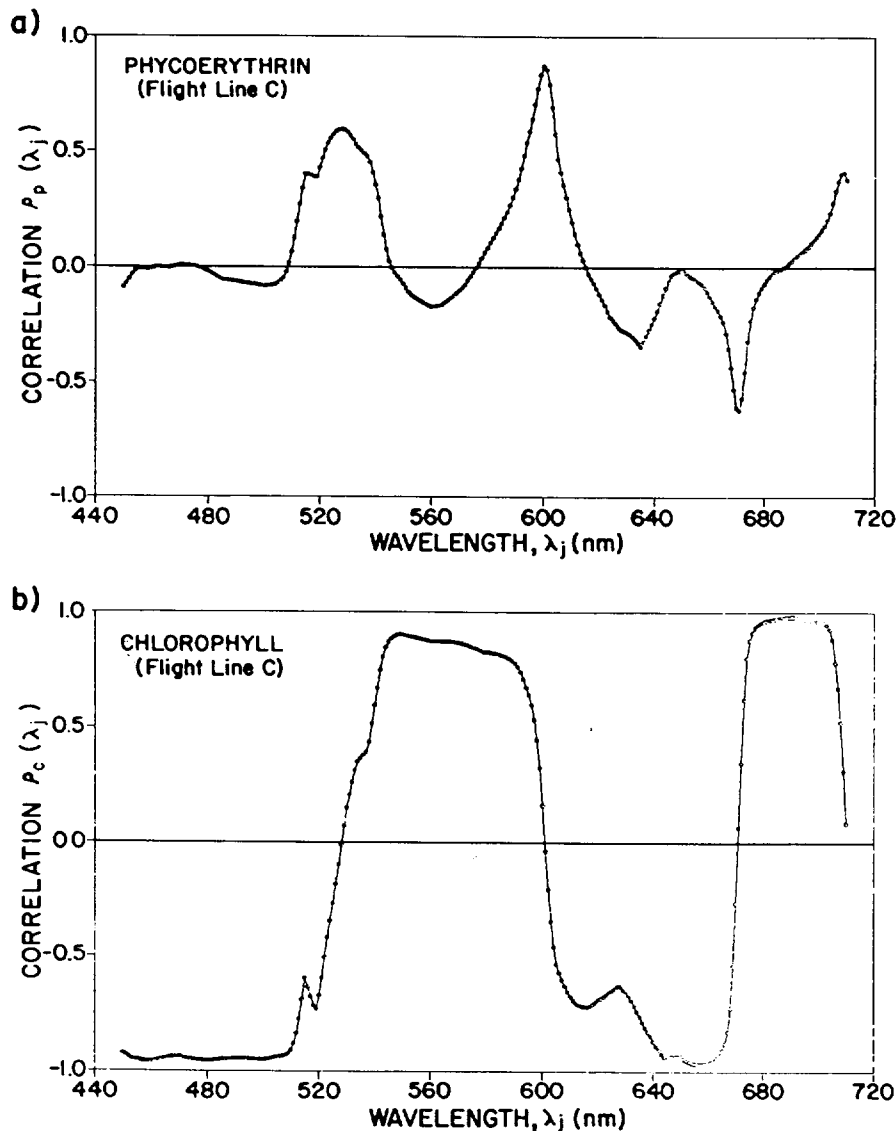


Figure 2. a) Example of spectral correlation for phycoerythrin,  $\rho_p(\lambda_i)$  for Flight Line C of Figure 1. Note the correlation peak at  $\sim 600$  nm. b) Corresponding spectral correlation for chlorophyll,  $\rho_c(\lambda_i)$ . Throughout this paper, the passively derived chlorophyll comparisons are obtained from the  $\sim 650$  nm chlorophyll absorption region.

found in the 530 nm region (Yentsch and Yentsch, 1979). It may be due to covariability with other phytoplankton pigments whose functions are coupled to those of phycoerythrin. For example, the phycocyanin absorption peak is much closer to 600 nm than is the phycoerythrin. Thus, it is possible that only phytoplankton species containing both phycocyanin and phycoerythrin are being detected. That is, the laser is stimulating and measuring the phycoerythrin fluorescence while the passive upwelled radiances could be measuring the effects of the phycocyanin pigment. In order to test this hypothesis (as well as establish the wavelengths of color bands for its eventual satellite measurement), efforts are now underway by our group to conduct airborne field experiments with an additional laser wavelength at  $\sim 600$  nm in order to obtain the phycocyanin fluorescence in the 650 nm region. On alternating laser pulses, the 532 nm laser radiation would be emitted to stimulate phycoerythrin and thus identify regions of coexistence with phycocyanin pigment.

The environmental factors that somehow combine to occasionally reduce the chlorophyll domination of the upwelled spectra at the 600 nm wavelength is at present unknown. The high chlorophyll correlation in the 690 nm region is caused by the chlorophyll fluorescence emission (Hoge and Swift, 1986a,b). Likewise the high correlation in the  $\sim 660$  nm region is attributed to chlorophyll absorption. It is from this latter spectral region that all the chlorophyll profile plots will be extracted for consideration.

## DESCRIPTION OF RESULTS

We have selected flight lines from four airborne missions to demonstrate that phycoerythrin pigment affects the underwater light field. In fact, the results from these missions suggest that the ocean color spectrum is influenced to the degree that the phycoerythrin concentration can be reasonably estimated from passive ocean spectral measurements.

Flight Lines A and B (Fig. 1) were obtained during the conduct of two missions flown to provide validation data for the CZCS sensor during August 1984. Flight Line C was acquired during the Department of Energy Shelf Edge Exchange Processes (SEEP) experiment (Walsh et al., 1986)

in April 1984. Flight Line D was acquired during an instrument checkout mission flown prior to participation in the U.S. Office of Naval Research BIOWATT II experiment during August 1987. The locations of the respective flight lines are shown in Figure 1. Additional information about the flight lines and instrument configuration differences between the flight lines can be found in Table 2.

We will use essentially the same format for the presentation of results from all four mission flight lines. For phycoerythrin recovery we used the curvature algorithm of Eq. (4) with  $-\log G_w(\lambda_j)$  centered very near to 600 nm. For chlorophyll recovery high correlation coefficients between  $-\log G_w(\lambda_j)$  and laser-induced chlorophyll fluorescence were obtained in several spectral regions. High negative correlation was found in the characteristic blue spectral region as well as near 665 nm while an elevated region of positive correlation was found near 690 nm. The peak (negative) correlation in the 645–665 nm spectral region was selected for demonstrating that the ocean color spectra contained strong chlorophyll influence because this region provided the best overall correlation for the entire group of Case II water masses utilized in these analyses.

### Flight Line A

Flight Line A was flown during August 1984 along the New Jersey coast line. As shown in Figure 1, the flight line was oriented roughly parallel to the shoreline at a distance of 3–5 km offshore. Approximately 8750 pulsed laser-induced spectra and 8750 passive ocean color spectra were acquired and used in the analysis of this flight line.

Figure 3a shows the water-Raman-normalized, laser-induced phycoerythrin and chlorophyll fluorescence profiles plotted as a function of time. The values of both fluorescence profiles are given as dimensionless numerical ratios resulting from the normalization of the respective fluorescence with the water Raman backscatter signal. Figure 3a facilitates direct visual comparison of the relative strength and the noncoherency of the two pigments along a specific flight line. At the nominal 100 m/s velocity of the P-3A aircraft, the 1600 s span of data shown in the profile cross section represents a distance of approximately 160 km. The degree of noncoherence between the phyco-

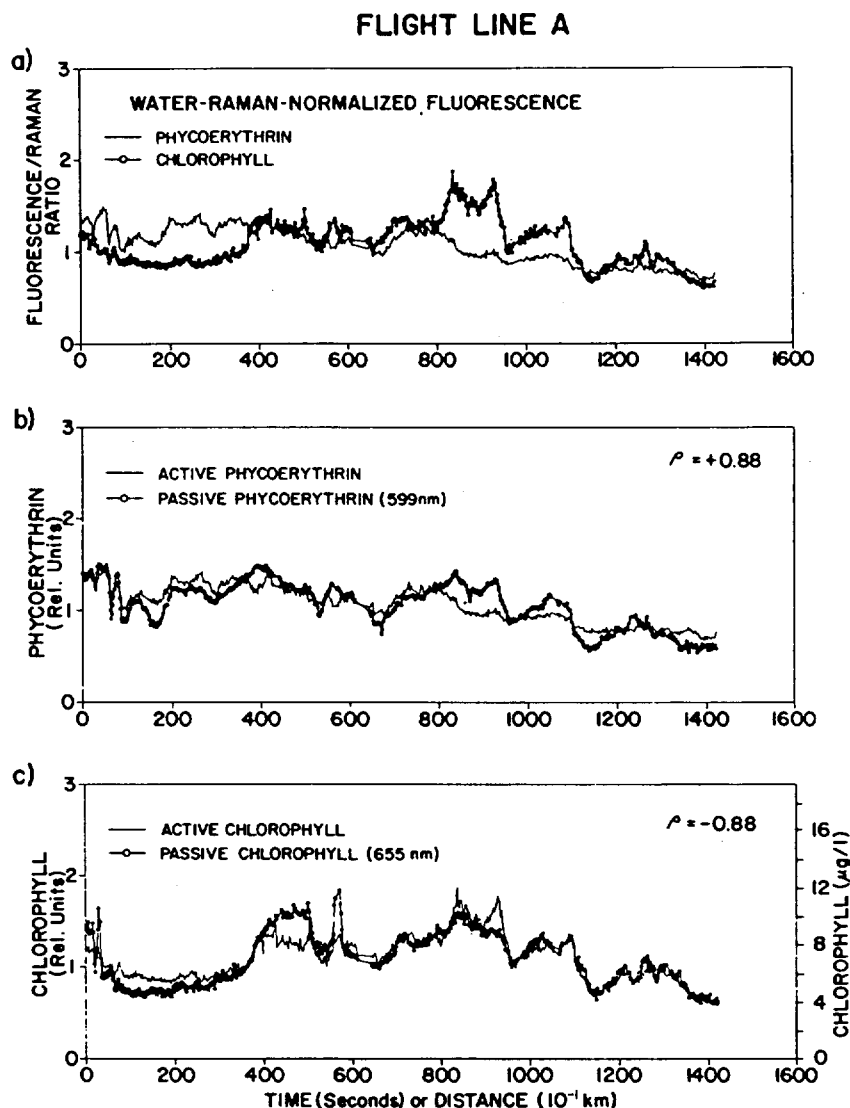


Figure 3. a) Normalized phycoerythrin and chlorophyll fluorescence showing the required noncoherency of the two pigments along Flight Line A. b) Along-track comparison of passive phycoerythrin obtained with 599 nm center-band curvature algorithm and the laser-induced and water-Raman-normalized phycoerythrin fluorescence obtained along Flight Line A. c) Along-track comparison of passively derived chlorophyll and the normalized laser-induced chlorophyll fluorescence obtained along Flight Line A. The chlorophyll concentration range was determined from the *in situ* ship truth along the flight line.

erythrin and chlorophyll profiles, which is required for unambiguous active-passive correlation analysis, is evident in Figure 3a, especially near the beginning of the flight line. From a correlation spectrum similar to the one in Figure 2a, it was found that the laser-induced and water-Raman-normalized phycoerythrin fluorescence was best recovered with a curvature algorithm  $-\log G_w$  (599) centered at 599 nm ( $\rho = 0.88$ ). The passive phycoerythrin along-track profile for this algorithm is plotted in Figure 3b together with the laser-

induced and water-Raman-normalized phycoerythrin.

The concurrent recovery of the normalized chlorophyll fluorescence with a passive curvature algorithm centered at 655 nm is shown in Figure 3c. The profiles of both pigments recovered from the passive ocean color spectra show reasonable agreement with their corresponding laser-induced fluorescence profile over the entire flight line. Note the performance of the respective algorithms along sections of the flight line where the chloro-

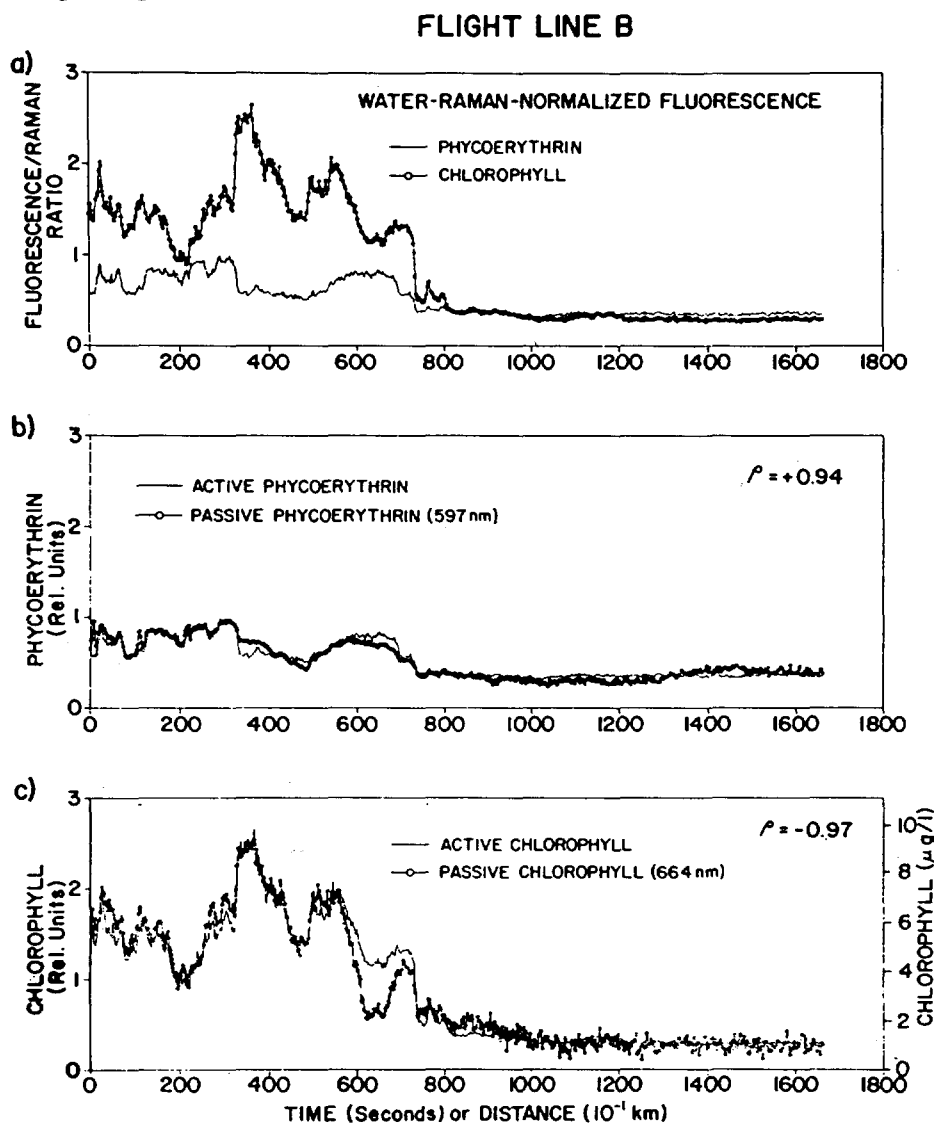
phyll and phycoerythrin pigments exhibit the strongest noncoherence such as in the initial 400 s. The pigment estimates from upwelled radiances generally follow the trend of the respective laser induced fluorescence profiles; however, systematic differences between the active and passive estimates of the pigments are also apparent at some locations. Ship truth was available along this line and the range of chlorophyll concentration is given on the righthand scale of Figure 3c (Hoge et al., 1987). The ship truth values are plotted with large

symbols within Figure 3c. In general the ship truth was in good agreement with the airborne data. Deviations are attributed to a spatial separation (between aircraft and ship) of 4–10 km and time differences of 0–12 h (Hoge et al., 1987).

### Flight Line B

Flight Line B was also flown during August 1984. As shown in Figure 1, the flight line paralleled the Virginia coast, crossed the Chesapeake Bay mouth,

**Figure 4.** a) Normalized phycoerythrin and chlorophyll fluorescence showing the noncoherency of the two pigments. b) Along-track comparison of passive phycoerythrin obtained with 597 nm center-band curvature algorithm and the normalized laser-induced phycoerythrin fluorescence for Flight Line B. c) Along-track comparison of passively derived chlorophyll and the normalized laser-induced chlorophyll fluorescence for Flight Line B. The chlorophyll concentration range was determined from the in situ ship truth obtained along the flight line.



and then proceeded in a southeasterly direction across the inner portion of the shelf. The segment of the flight line along the Virginia coast was flown within 5 km of the beach. The Bay mouth crossing was conducted in order to obtain active-passive ocean color observations from a variety of water masses. The phytoplankton activity is largely restricted to the Case II coastal water and bay outflow plume contained in the initial 750 s of the flight line. Depressed offshore levels of the pigments is typical for mid-August. Approximately 10,300 laser-induced spectra and 10,300 passive ocean color spectra were acquired and used in the analysis of this flight line.

The results from the analysis of Flight Line B are shown in Figure 4 using the same format described in the discussion of Figure 3. The water-Raman-normalized laser-induced phycoerythrin and chlorophyll fluorescence profiles are plotted in Figure 4a as a function of time or distance in order to depict the noncoherence of these two pigments. Extensive sections exhibiting the requisite noncoherence are apparent in the first 750 s of the flight line.

The curvature algorithm with the center band at 597 nm was found to provide the highest correlation with laser induced phycoerythrin fluorescence. The  $-\log G_w(597)$  values are shown plot-

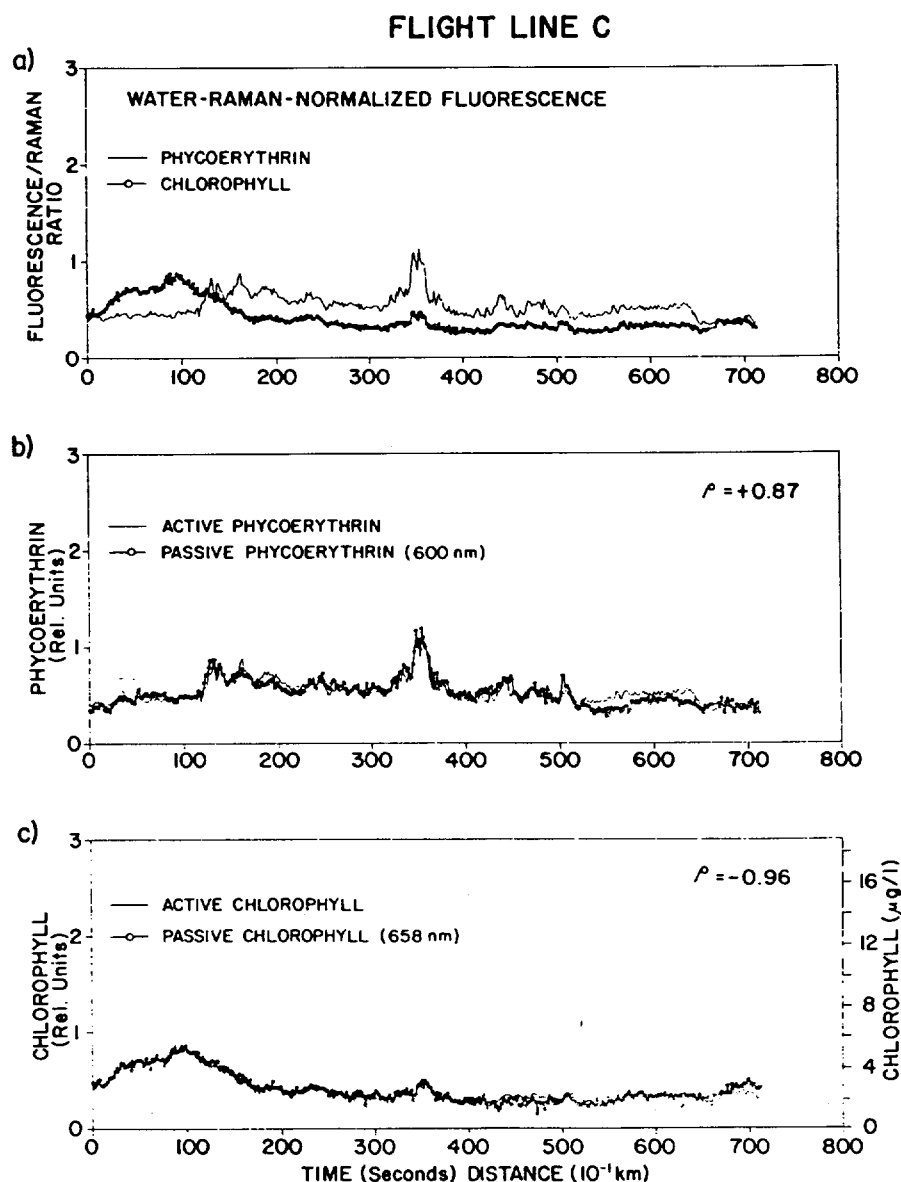


Figure 5. a) Normalized phycoerythrin and chlorophyll fluorescence profiles showing the required noncoherence along Flight Line C. b) Along-track comparison of passive phycoerythrin obtained with 600 nm center-band curvature algorithm and the laser-induced phycoerythrin fluorescence for Flight Line C. c) Along-track comparison of passively derived chlorophyll and the normalized laser-induced chlorophyll fluorescence for Flight Line C. The chlorophyll concentration range was determined from *in situ* ship truth data taken along the flight line.

ted in Figure 4b along with the laser-induced and water-Raman-normalized phycoerythrin fluorescence profile.

The best passive chlorophyll estimate was recovered from the curvature algorithm with the center band at 664 nm. The resulting  $-\log G_{\omega}$  (664) values are shown plotted in Figure 4c along with the laser-induced and water-Raman-normalized chlorophyll fluorescence profile. The chlorophyll concentration given along the rightmost ordinate was obtained from ship truth data (Hoge et al., 1987). Again, the estimates of the two pigments from the passive spectra are in reasonable agreement with their respective laser-induced fluorescence profiles in both Figures 4b and 4c,

but sections where the passive estimates systematically disagree with the fluorescence measurements are also apparent.

### Flight Line C

Flight Line C was flown in the New York Bight during April 1984 as part of the Shelf Edge Exchange Processes (SEEP) experiment. Ocean color spectra obtained on other flight lines from this field experiment had previously yielded good correlation between laser-induced chlorophyll and phycoerythrin fluorescence and estimates of the two pigments using the three-band spectral curvature algorithm (Hoge and Swift, 1986a). The water

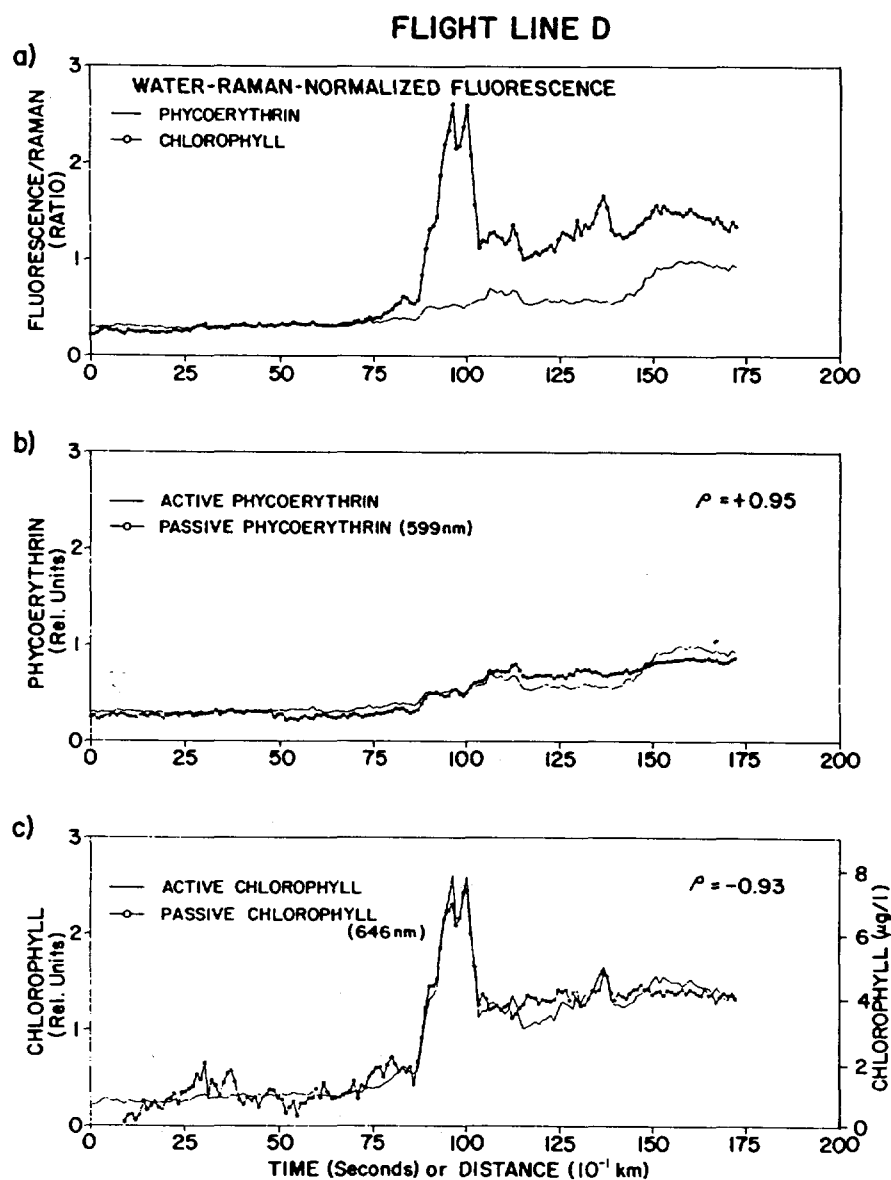


Figure 6. a) Normalized phycoerythrin and chlorophyll fluorescence profiles showing the requisite noncoherency along Flight Line D. b) Along-track comparison of passive phycoerythrin obtained with 599 nm center-band curvature algorithm and the laser-induced phycoerythrin fluorescence for Flight Line D. c) Along-track comparison of passively derived chlorophyll and the normalized laser-induced chlorophyll fluorescence for Flight Line D.

type on this flight line is felt to have a higher percentage of Case I water (Gordon and Morel, 1983) than the other flight lines discussed in this paper. Approximately 4375 laser-induced spectra and 4375 passive upwelled spectral radiances were acquired and used in the analysis of this flight line.

The results from the analysis of the data from Flight Line C are presented in Figure 5 using the same format adopted for the previous two flight lines. A large degree of noncoherence between the laser-induced phycoerythrin and chlorophyll fluorescence profiles is obvious in Figure 5a, especially in the initial 200-s segment and in the section between 300 and 400 s.

The passive  $-\log G_w(594)$  estimate of phycoerythrin shows excellent agreement in Figure 5b with the laser-induced phycoerythrin fluorescence over the entire flight line with only relatively minor systematic departures. The corresponding chlorophyll estimate from the curvature algorithm with center channel located at 661 nm shows rather good agreement with the laser induced chlorophyll fluorescence in Figure 5c. The chlorophyll concentration is given in the rightmost ordinate of Figure 5c based on shipboard measurements (Walsh et al., 1986).

### Flight Line D

Flight Line D was flown in August 1987 in the Atlantic Ocean off Assateague Island, Virginia. The flight track is oriented nearly perpendicular to the coastline and traverses approximately 18 km of the inner shelf. Approximately 1750 laser-induced spectra and 1750 passive upwelled radiance spectra were acquired and used in the analysis of this flight line.

Again, to demonstrate the non-coherence of the pigments, Figure 6a shows the water-Raman-normalized, laser-induced phycoerythrin and chlorophyll fluorescence profiles plotted as a function of time.

The highest correlation between pigment estimates computed with the three-band curvature algorithm and laser-induced phycoerythrin fluorescence occurred when the center band was located at 599 nm. The resulting active and passive phycoerythrin profiles are plotted in Figure 6b. The active and passive phycoerythrin profiles are in general agreement, although a disparity exists in the final 55 s of the pass.

The highest spectral radiance correlation with laser-induced chlorophyll fluorescence was found when the middle band of the curvature algorithm was centered at 646 nm. The active and passive chlorophyll profiles are plotted in Figure 6c. The passive chlorophyll profile follows the general trend of the active chlorophyll profile but numerous departures can be seen. The chlorophyll concentration given in the rightmost ordinate of Figure 6c is based on our experience with the fluorescence/Raman ratio in these waters.

### CONCLUSIONS

Considerable evidence has been presented to suggest that the submarine light field contains the scattering and absorption effects of the photosynthetic accessory pigment, phycoerythrin. The presence of the phycoerythrin pigment in the upper surface layer of the ocean was determined using established airborne laser-induced spectral fluorescence methods. Active-passive correlation spectroscopy techniques were then used to demonstrate that the simultaneously-measured water-leaving spectral radiances in the 597–600 nm region were highly correlated with the laser-induced phycoerythrin pigment fluorescence. In fact the radiances contained sufficient influence from the presence of phycoerythrin to permit the actual recovery of an estimate of the photopigment that was reasonably correlated ( $\rho = \pm 0.8$  or higher) with corresponding laser-induced phycoerythrin pigment fluorescence measurements.

In a number of other cases where the laser-induced chlorophyll and phycoerythrin profiles were noncoherent, the phycoerythrin pigment could not be recovered to a correlation value of better than  $\pm 0.8$ . In these circumstances, the correlation spectrum indicated that chlorophyll and/or other waterborne constituent optical effects had intruded into the 600 nm region.

The requisite noncoherence of chlorophyll and phycoerythrin pigment was determined from profile plots of the laser-induced and water-Raman-normalized pigment fluorescence. The quality of the passive ocean color spectra was validated by comparing the water-Raman-normalized chlorophyll fluorescence and the  $-\log G_w(\lambda)$  as computed with the spectral curvature algorithm. The chlorophyll was recovered from the  $\sim 650$  nm

spectral absorption region. It is interesting to note that the optimum chlorophyll recovery for the four separate passes varied from 646 to 664 nm, a span of 18 nm. For the same upwelled spectral radiance data, and using the same processing methods, the phycoerythrin recovery occurred over a smaller spectral interval, 597–600 nm or 3 nm. This suggests that the phycoerythrin influence is confined to a considerably more narrow spectral interval than chlorophyll absorption effects.

The curvature algorithm (Campbell and Esaias, 1983) was applied to the upwelled radiances to provide sensitive detection of the phytoplankton phycoerythrin pigment. During the course of the analysis several of the data sets were similarly processed using two-band radiance ratio algorithms. Findings indicated that two-band radiance ratios were not nearly as effective in recovering or estimating phycoerythrin. The tentative initial conclusion is that the phycoerythrin influences the passive ocean color spectra in such a way that the curvature is apparently affected more than the slopes of the spectra.

*The authors wish to extend their personal thanks to the many persons involved with the SEEP, NEMP-CZCS, and BIOWATT programs and field experiments, the AOL project team, and aircraft operations personnel. We also thank the Ocean Processes Branch of NASA Headquarters for their continued support and encouragement. The field support of Catherine Warsh of the NOAA Ocean Assessments Division is gratefully acknowledged.*

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